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Characterization of epoxy-graphite composites by diffuse reflectance FTIR

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Abstract

Diffuse reflectance Fourier transform infrared spectroscopy has been used to obtain IR spectra of epoxy-graphite prepregs and cured panels. The spectra are influenced by fibre orientation and front-surface reflection effects which limit the usefulness of the method for quantitative analysis. However, for qualitative work, excellent spectra can be obtained with practically no sample preparation.

Introduction

The rapidly growing use of fibre-reinforced organic-matrix composites in high-performance applications has been accompanied by an increasing interest in the development of rapid and reliable methods for assuring their quality and performance (1). Transmission infrared spectroscopy has proved of great value for both qualitative and quantitative characterization of the organic resins used (2,3). With the advent of interferometric instrumentation, diffuse reflectance infrared spectroscopy has become a more viable method (4), one of its main advantages being ease of sample preparation. In the case of composite "prepregs" (woven fabric reinforcement impregnated with partially cured epoxy resin), spectra can be measured on the prepreg as received, whereas transmission IR requires solvent extraction of the resin and casting of a thin film. Similarly, spectra can be obtained on cured composite parts which would require grinding to a fine powder for transmission measurements. Disadvantages of diffuse reflectance include complications arising from the importance of scattering and the presence of front-surface specular reflection effects. The work reported here was undertaken in order to study the importance of these effects and to explore the possibility of using diffuse reflectance for quantitative measurements on composite systems.

Experimental

The composite system studied was Rigidite 5208/WC3000 from Narmco, Inc. It consists of carbon-fibre woven fabric impregnated with resin based on a major epoxy (main component tetraglycidyl-4,4'-diaminodiphenylmethane, or TGDDM), a minor epoxy (glycidyl ether of a bisphenol-A Novolac), and an amine hardener (4,4'-diaminodiphenylsulphone, or DDS)(5). FTIR spectra were run on a Nicolet Model 170SX instrument equipped with a mercury cadmium telluride detector and a "praying mantis" diffuse reflectance accessory from Harrick Scientific Corp. Both uncured prepreg and cured panels were measured by cutting small squares (about 1 cm x 1 cm) and attaching them with double-sided adhesive tape to a flat horizontal support whose height could be adjusted to maximize overall reflectivity with respect to the reference material used (powdered infrared-grade potassium bromide, compacted with a spatula). Spectra were recorded using 128 scans requiring a total of 80 seconds.

Results and Discussion

The fabric used in the samples studied was based on an 8-harness satin weave pattern, in which each fill yarn passes alternately over seven warp yarns and under one. Consequently, on a given prepreg surface, seven-eighths of the total area is covered by fibres aligned in one particular direction, which will be called the "principal fibre direction". Figure 1 illustrates the effect on the DR (diffuse reflectance) spectrum of changing the principal fibre direction with respect to the beam propagation direction of the instrument. The spectra obtained using the "parallel" orientation are of much higher spectral contrast, for both uncured prepreg and cured panels, and all subsequent spectra were run using this orientation. In spite of a strong background absorption due to the carbon fibres, high-quality spectra are obtained for the

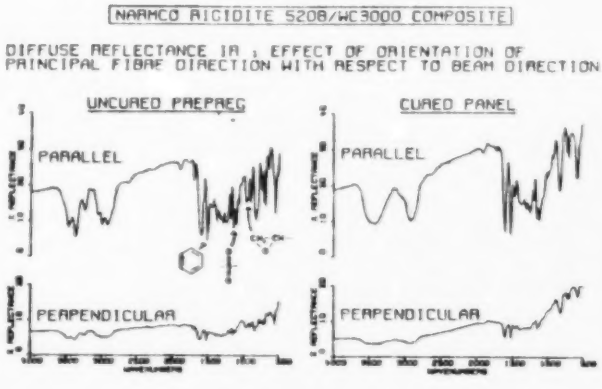

Figure 1

epoxy resin. Particularly interesting features are the strong aromatic ring band at 1520 cm^{-1}, bands of the DDS sulphone group at 1147 and 1107 cm^{-1}, and bands arising from unreacted epoxy rings in the 1000-900 cm^{-1} region. The latter disappear on curing of the resin and can be used as an indicator of the completeness of cure. Hence, diffuse reflectance can be used to confirm completeness of cure without destruction of the sample.

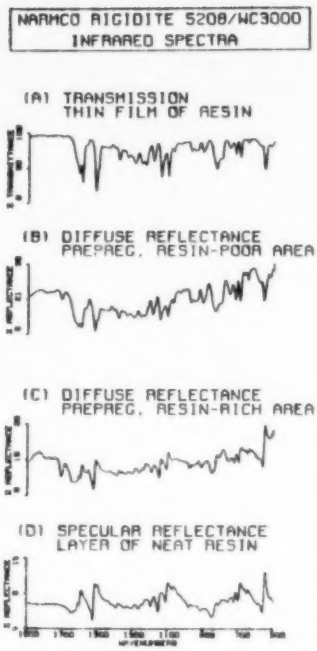

Figure 2

Comparison of several DR spectra with transmission spectra showed some variation in band shapes which can be attributed to front-surface reflection effects, as shown in Figure 2. Figure 2(a) is a transmission spectrum measured for a thin film of resin extracted with acetone and deposited on a KBr window. Figure 2(d) is a front-surface reflection spectrum obtained for the same sample using a Harrick External Specular Reflection Accessory (angle of incidence 30°). The shape of the latter spectrum is determined largely by the influence of refractive index dispersion and is quite different from the transmission curve, which is determined mainly by the absorption coefficient. Figures 2(b) and 2(c) show DR spectra obtained at two different points on the prepreg surface, one rich in resin and one poor. In both cases, comparison with the transmission spectrum shows that the bands are "deformed" by specular reflection effects. The effect is greater for the resin-rich area because there are fewer fibres near the surface to properly diffuse the incident radiation.

It has been reported recently (6,7) that the quality of DR spectra of polymer and fibre surfaces can be improved by using an overlayer of powdered KBr to reduce specular reflection and produce more isotropic scattering. This technique was applied to the prepreg. It was found that sprinkling with a light layer of KBr had little beneficial effect and only reduced the spectral contrast. However, when a layer of KBr was pressed into the prepreg using finger pressure, then inverted and tapped to shake off the excess, better results were obtained. Band shapes were more reproducible and the importance of sample orientation was greatly reduced (i.e. the scattering became more isotropic). The possibility of using this technique for quantitative purposes was investigated as follows. A set of spectra was recorded for seven squares cut from the same lot of prepreg, and then converted to Kubelka-Munk units $f(R) = (1-R)^2/2R$, where R is the reflectance (4). (Although the K-M theory applies to powders, it was found that the spectra obtained using this conversion bore a closer resemblance to absorbance spectra recorded in transmission than did DR spectra converted to absorbance.) Using Nicolet software, integration of the following bands was performed between the limits indicated: aromatic ring (1552-1486 cm^{-1}), sulphone (1165-1046 cm^{-1}), epoxy (995-874 cm^{-1}). The latter two were then ratioed against the first to give a "sulphone index" (related to the total content of DDS) and an "epoxy index" (related to the unreacted epoxy content). The respective values and standard deviations obtained were 1.86 ± 0.14 (7.4%) and 1.48 ± 0.35 (23%). It appears that the DR method is of limited value for quantitative analysis of composites, in view of the poor reproducibility. In transmission, with careful sample preparation, a precision of 2% is readily achieved. The poor reproducibility in DR is no doubt due to the incomplete elimination of specular reflection effects and possibly to variations in the scattering coefficient "s" which influences the spectra (4).

Conclusions

Diffuse reflectance infrared spectroscopy is a very useful technique for "as is" qualitative analysis of fibre-reinforced epoxy prepregs and composites, but is of limited usefulness for quantitative analysis.

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